Rings of light

The atomic structure of the bacterial light-harvesting complex helps to explain how the energy of sunlight is efficiently absorbed and transferred between bacteriochlorophyll molecules towards the reaction centre.

The absorption of light energy by chlorophyll pigments is the first step in photosynthesis. Subsequently, this energy is converted into a photochemical form by reaction centres and ultimately it is used to convert carbon dioxide into carbohydrate. All photosynthetic organisms, whether bacteria or plants, need to ensure that sufficient energy is available to drive these biosynthetic processes. This is achieved by surrounding reaction centres with perhaps a one-hundred-fold excess of pigments, each held in a specific position by proteins (which in purple photosynthetic bacteria and plants are intrinsic membrane proteins). Such a combination of pigments and proteins is referred to as a light-harvesting complex. In bacteria the dominant complex is LH2, which donates energy to a second complex, LH1; LH1 surrounds and interconnects the reaction centres, which are the sites at which the photochemical reaction occurs.

Our understanding of the process by which such pigment-proteins absorb light energy and transmit it with high speed and efficiency to the reaction centre has been significantly advanced by the recent work of McDermott *et al.* [1], who reported the atomic structure of a bacterial light-harvesting complex. One representation of the structure is shown in Figure 1a, in which the bacteriochlorophyll and carotenoid pigments are seen in isolation, without any polypeptides present. There are 18 bacteriochlorophyll molecules (green) that maximally absorb light of wavelength 850 nm, and these form an overlapping ring, in which each B850 pigment molecule is closely associated with its neighbouring pigment. These 18 molecules are positioned vertically with respect to the membrane plane, in contrast to the B800 pigments (blue in Fig. 1a), which lie towards the cytoplasmic face of the membrane and almost parallel to it.

The phytol chain of each bacteriochlorophyll can also be seen in Figure 1a, which shows how these chains of the B850 and B800 pigments intertwine. This kind of association has also been seen in the bacterial reaction centre, in which there are two apparently symmetrical branches of pigments; the interactions between the phytol chains are more pronounced in the 'active' branch [2], and the significance of this phenomenon for the transfer of both energy and electrons will be of interest in future work. Finally, there are nine membrane-spanning carotenoids (white in Fig. 1a), each of which spans the membrane and in so doing makes close contact (less than 3.5 Å) with both the B850 and B800 bacteriochlorophylls. These pigment molecules form two distinct rings, which can be seen in the views of the periplasmic (Fig. 1b) and cytoplasmic (Fig. 1c) faces of the complex. Moreover, the contacts between the bacteriochlorophylls have been emphasized, so much so that in Figure 1b the impression is gained of a single, circular 'supermolecule' of B850 bacteriochlorophylls.

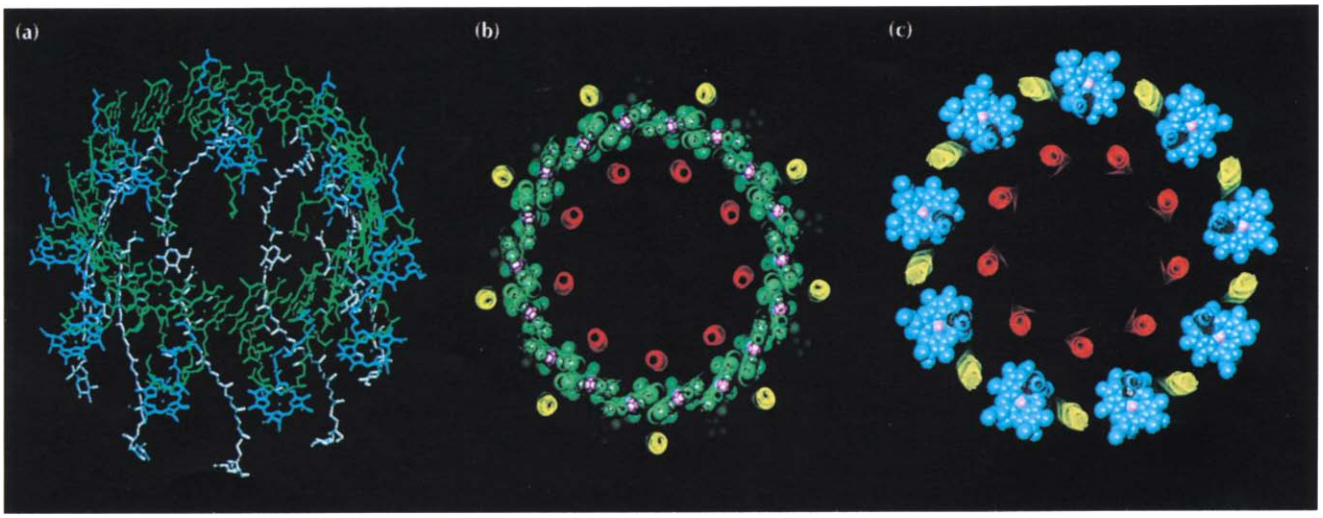

Fig. 1. The ring of bacteriochlorophyll and carotenoid pigments in the LH2 light-harvesting complex viewed from **(a)** the side of the molecule, carboxyl terminus towards the top; **(b)** the periplasmic face; **(c)** the cytoplasmic face. The B800 molecules are in blue, and the B850 molecules in green; the magnesium atoms are coloured purple. In (b) and (c), the α and β subunits are viewed end-on, coloured in red and yellow, respectively. These models were built from the electron density maps using the program 'O' [10].

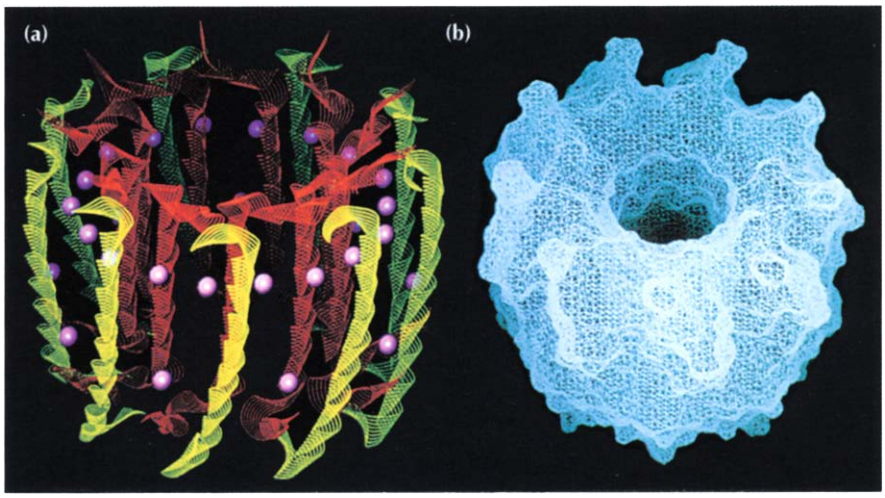

Fig. 2. **(a)** A representation of the LH2 complex showing the α and β polypeptide subunits and the magnesium atoms within the bacteriochlorophyll molecules as spheres, to emphasise the ring-like arrangement of the pigments. The carboxyl terminus is at the top. **(b)** The LH2 complex represented with a 'surface', so that its overall shape can be seen. The carboxyl terminus is at the top. The program 'GRASP' [11] was used for this representation of the structure.

The polypeptides that hold these molecules in position are themselves in a circular arrangement with a nine-fold symmetry. The B850 molecules are sandwiched between the helices of the α and β polypeptide subunits, each of which provides one alternating histidine ligand for each pigment. The binding site for B800 is formed by coordination of the magnesium atom by the amino-terminal formyl-methionine residue from the α subunit, as well as by an interaction of this magnesium atom with the βHis_{-18} residue (where His_0 is defined as the residue that forms the ligand of the B850 pigment) via a water molecule, and of the macrocycle with Arg_{-10} through a hydrogen bond.

The relative levels of LH2 complexes and LH1–reaction centre cores vary, depending on environmental factors such as oxygen tension and light intensity. As the structure reveals, LH2 complexes are superbly well-designed for the task of absorbing light energy, either in the visible region of the spectrum (from 400–600 nm) using bacteriochlorophyll and carotenoid pigments or in the 800–900 nm region, again using the bacteriochlorophyll absorbance bands, at 800 and 850 nm. The distance between B800 and B850, on either the α or the β subunit, is sufficiently close (a minimum of 17.6 Å between magnesium atoms) to allow the transfer of energy in 0.7 picoseconds. Moreover, the distance from the carotenoid molecules to either B800 or B850 is also sufficiently close to facilitate rapid transfer to either bacteriochlorophyll molecule. As a result of such transfers, excitation energy will arrive at a B850 molecule either by direct absorption or from the other pigment molecules.

It is at this point that the significance of the ring structure becomes apparent, as the inherently random nature of the incident radiation and of the subsequent absorption and transfer of light energy is reduced to a two-dimensional process involving transfer round the ring. The close association between the 18 B850 molecules (Fig. 1) ensures that this transfer is extremely rapid — sufficiently so that the time taken by an excited state to visit all 18 probably does not exceed 5 picoseconds. Thus, the point of contact that an LH2 ring makes with a neighbouring LH1 complex is unimportant, since the energy will simply jump between the two nearest bacteriochlorophyll molecules in different rings. This distance is probably around 30 Å, and is compatible with the transfer time of approximately 5 picoseconds that has been estimated using the latest two-colour subpicosecond laser spectroscopy techniques (S. Hess, M. Chachisvilis, K. Timpmann, M.R. Jones, C.N.H and V. Sundström, unpublished observations). In Figure 2a, the LH2 complex is shown with the pigments represented as spheres; this helps to reveal the existence of the two rings of pigments, one of B800 and the other of B850.

Figure 2b shows the LH2 complex in such a way as to give some impression of its biologically relevant size and shape. As a result of the 8.5 Å resolution projection map of the LH1 complex from *Rhodospirillum rubrum*, which depicts this complex as a 16α:16β structure [3], it is not unreasonable to assume that LH1 could also form a circular structure *in vivo*. If it obeys the same imperatives as LH2, we may also assume that the 32 B875 bacteriochlorophylls are again arranged in an overlapping ring, and that these pigments are positioned at the same level in the membrane as the pigments in LH2. This, in turn, would be at the same level as the reaction centre 'special pair' of bacteriochlorophylls, where the photochemical reaction is initiated. Thus, the overall design of the bacterial photosystem becomes easier to understand: the delocalization of energy round the LH2 B850 ring reduces the need for any specific orientation of LH2 with respect to LH1, and furthermore the efficiency of transfer between rings is maximized by movement along a level plane to the reaction centre special pair. Thus, the light-harvesting rings, apart from being subjectively beautiful to look at, are also superbly well-adapted to their function.

This advance in our knowledge of the molecular details of this light-harvesting complex should stimulate experiments designed to examine the role played by various amino-acid residues in the LH subunits, and to examine how the LH2 structure obtained *in vitro* relates both to the native, membrane-bound LH2 complex *in vivo* and to the LH1 complex. Such possibilities are enhanced by

the rapid parallel development in spectroscopic techniques. For example, Fourier transform resonance Raman spectroscopy has been able to reveal fine details of LH structures by, for example, measuring the effects that hydrogen bonds can exert on the C2 acetyl and C9 keto carbonyl groups of bacteriochlorophyll *a* — thus, tyrosine residues were revealed as participants in such bonds within LH2, by site-directed mutagenesis of phenylalanine and leucine residues [4]. Furthermore, the time resolution available for the study of energy transfer events in such complexes has increased sharply in the last six years or so, with 20–30 femtoseconds routinely within reach. As a result, very early events that follow the absorption of a photon by a bacteriochlorophyll — such as the relaxation between excitonic states — and coherent phenomena in which the excited state appears to oscillate [5] in a manner also seen for membranes containing reaction centres [6], can be examined in the light of this new structural information.

The light-harvesting complexes still have a lot of secrets to reveal: the precise way in which they can 'red-shift' the bacteriochlorophyll absorbance peak by up to 100 nm; the self-association properties that determine the ring structure and the extent of its oligomerization to an $(\alpha\beta)_9$ structure; and the way in which these properties allow extended energy transfer networks to form. Thus, future developments will continue to be at the forefront of biological and physical research. Coming so soon after the atomic-resolution model of the plant light-harvesting LHCII structure from Werner Kuhlbrandt's group [7], the work by McDermott *et al.* [1] provides almost an embarrassment of riches for photosynthesis research, especially as the two light-harvesting complexes constitute one third of all known membrane protein structures that have been determined to atomic resolution — and even more so given that one of the other membrane protein structures is the recipient of the harvested energy, the bacterial reaction centre [2]. Taken together with the structures of other light-harvesting complexes, the water-soluble bacteriochlorophyll *a* protein from *Prosthecochloris aestuarii* [8] and the cyanobacterial phycobilisome proteins [9], this latest work can be viewed as 'completing the set' of light-harvesting complexes. These are exciting times for those who work in this field.

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